ABOUT THE USE OF LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR THE DETERMINATION OF FUNDAMENTAL SPECTROSCOPIC PARAMETERS

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1. INTRODUCTION

The laser-induced breakdown spectroscopy (LIBS) technique is known as a flexible analytical technique, which has been widely used since more than 40 years in many fields of application, mainly because of its speed, versatility and (apparent) simplicity [Cremers 2013].

In many LIBS applications, the analytical results are often coupled with plasma diagnostics, usually based on simplifying assumptions of thermal equilibrium and plasma homogeneity, for the determination of the main plasma parameters, namely electron temperature and electron number density [Tognoni 2006].

For the determination of those parameters, the knowledge is needed on the fundamental spectroscopic parameters of the emission lines observed in the LIBS spectrum, namely the energies E_k and E_i of the upper and lower levels of the transition, the degeneracies of the levels, g_k and g_i, respectively, the temperature-dependent partition function of the species $U(T)$, the transition probability A_{ki} and the Stark coefficient of the line.

While the first parameters are linked to the intensity of the light emitted in the transition and the number concentration of the emitting species, the latter is only related (in the first approximation) to the shape of the emission line. In fact, in the LTE approximation and for an homogeneous and optically thin plasma, the light intensity emitted at the frequency $(E_k - E_i)/h$, with h = Planck constant, can be expressed through the Boltzmann equation:

$$I_0 = F n^a g_k A_{ki} \frac{e^{-\frac{E_k}{k_B T}}}{U^a(T)}$$

$$a = \begin{cases} I & \text{for neutral lines} \\ II & \text{for ionized lines} \end{cases} \tag{1}$$

where n^a is the number density of the emitting species, k_B is the Boltzmann constant, T is the plasma temperature and F is a scale factor depending on the efficiency of the experimental apparatus. On the other hand, in the first approximation the Full Width at

Half Maximum (FWHM) $\Delta\lambda_0$ of the emission line can be associated to the electron number density n_e of the plasma using the relation:

$$\Delta\lambda_0 = \omega_s \, n_e \tag{2}$$

The proportionality between $\Delta\lambda_0$ and n_e through the ω_s coefficient assumes as the only broadening mechanism in the plasma the perturbation on the atomic energy levels given by the electric field of the free electrons in the plasma. This kind of broadening is called *Stark broadening* [Griem 1976], and gives to the LIBS researchers a conceptually simple tool for determining the electron number density from the knowledge of the ω_s parameter and the measure of the FWHM of an emitting line, in the same way as eq.(1) allows the determination of both the number concentration of the emitting species and the plasma temperature through the knowledge of the partition function of the species $U(T)$ and E_k, g_k, and A_{ki} for at least two emission lines of the same species [Ciucci 1999].

From the knowledge of the spectroscopic parameters of the LIBS lines is thus possible (using eq. (1) and (2) and under some simplifying hypotheses) to obtain the electron temperature and electron number density of the plasma. Several researchers noticed that, if eq. (1) and (2) would give a correct description of the physics of the LIBS plasma, an independent determination of the plasma temperature and electron number density would allow to obtain the spectroscopic parameters (mainly the transition probabilities A_{ki} and the Stark coefficient ω_s, which are the most problematic to measure or to determine theoretically) [Aberkane 2020].

Surprisingly enough, while it is commonly agreed among the plasma physicists and chemists that eq.(1) and (2) (and consequently, the approximation of homogeneous plasma in LTE conditions) describe well the LIBS plasmas in some temporal interval during the plasma evolution, as demonstrated by many results in the literature, the same equations are strongly questioned when they are applied to the determination of the fundamental spectroscopic parameters.

The point which is most criticized is the use of the homogeneous plasma approximation, which is assumed for modelling the plasma by eq. (1) and (2). However, under this objection there is often an underlying concern, typical of the old plasma school, of making the things 'too easy' by the use of LIBS, when the experimental determination of the fundamental spectroscopic parameters typically requires extremely complex strategies when traditional methods are applied.

Two consideration can be done about these concerns. The first is that the measurement of the fundamental spectroscopic parameters of the LIBS emission lines is not easy at all, and requires the same skill and knowledge, if not more, that the traditional methods. The second, quite obvious, is that the results obtained by LIBS can be easily compared with that obtained by traditional methods; when the results coincide, within the experimental errors, few objections can be further raised.

There is another way to demonstrate the feasibility of LIBS for the purpose, which is to simulate numerically some extreme non-ideal plasma conditions and discussing how these non-ideal conditions reflect on the experimental determination of the fundamental spectroscopic parameters. This is the approach that we have taken, and that we will discuss in this communication.

2. EXPERIMENTAL

The numerical experiment that we will describe assumes a plasma in LTE conditions but takes into full account the possibility that the plasma would not be optically thin at the wavelength of the transition. Moreover, the plasma can be non-homogeneous in both the electron temperature and the electron number density. The plasma emission is simulated through the numerical solution of the radiative transport equation [Rezaei 2020]:

$$\frac{dI(\lambda,x)}{dx} = \varepsilon(\lambda,x) - k(\lambda,x)I(\lambda,x) \tag{3}$$

$\varepsilon(\lambda,x)$ is the contribution of the spontaneous emission:

$$\varepsilon(\lambda,x) = B(\lambda,x)\, k(\lambda,x) \tag{4}$$

and $B(\lambda,x)$ is the Planck black body radiation function. $k(\lambda,x)$ represents the effect of the absorption and stimulated emission:

$$k(\lambda,x) = \frac{\lambda_0^4}{8\pi c} A_{ki} g_k \frac{n_i(x)}{g_i}\left(1 - \frac{n_k(x) g_i}{n_i(x) g_k}\right) L(\lambda,x) \tag{5}$$

n_i is the population of the lower level of the transition, while n_k is the population of the upper level. The population of the levels may vary with the x coordinate within the plasma, because of the possible inhomogeneity of the electron temperature and number density.

The shape of the emission lines is assumed to be described, as usual in LIBS analysis, by the Lorentzian function:

$$L(\lambda) = I_0 \frac{\frac{\Delta\lambda_0}{2\pi}}{(\lambda-\lambda_0)^2 + \left(\frac{\Delta\lambda_0}{2}\right)^2} \tag{6}$$

where I_0 is the line integral intensity and λ_0 is the central wavelength of the line.

The analysis of the simulated spectrum for the determination of the fundamental spectroscopic parameters is then performed as in the case of 'true' experimental data.

In particular, to evaluate the optical thickness of the plasma we used a method developed by our laboratory in Pisa in 2005 [El Sherbini 2005], and largely validated in the following years [Bredice 2007, Safi 2019] which links the self-absorption parameter

SA, defined as the ratio between the peak emission of the self-absorbed line over the equivalent peak intensity in the absence of self-absorption, to the measured integral intensity of the line and the line FWHM as:

$$I = I_0\ (SA)^{0.46} \tag{7}$$

$$\Delta\lambda = \Delta\lambda_0\ (SA)^{-0.54} \tag{8}$$

From eq. (5), the parameter SA can be written as

$$SA = \frac{1 - e^{-k(\lambda_0)l}}{k(\lambda_0)l} \tag{9}$$

where l is the length of the optical path of the radiation in the plasma.

A consequence of eq. (8) is that, from the measurement of $\Delta\lambda$ and the knowledge of SA (from eq. (7), for example) one would be able to estimate $\Delta\lambda_0$ and, from eq. (2), the Stark broadening coefficient ω_s.

3. Results and discussion

The main results of the numerical simulation, corresponding to different plasma conditions and various degrees of inhomogeneity, are here summarized in the specific case of the determination of the Stark broadening parameters:

For optically thin plasmas ($k(\lambda_0)l \ll 1$) the effect of plasma inhomogeneity (both electron temperature and number density) on the determination of the Stark coefficient is almost negligible. This is because the determination of the Stark coefficient is experimentally done by comparing the broadening of the line with the one of a suitable (optically thin) reference line of known Stark coefficient. Since also the reference line broadening is affected by the plasma inhomogeneity in the same way, the overall effect on the evaluation of the Stark broadening effect is negligible;

For optically thick plasmas ($k(\lambda_0)l > 1$) the error on the Stark coefficient depends on the degree of inhomogeneity of the plasma. For a homogeneous plasma, eqs. (7) and (8) describe very well the plasma emission up to extreme values $k(\lambda_0)l \sim 20$. The presence of electron temperature and number density inhomogeneities minimally affects the evaluation of the Stark broadening coefficient, unless serious deformations of the lineshape occur (self-reversal). The self-absorption limit for the onset of self-reversal depend on the plasma inhomogeneity; however, self-reversal is easily recognizable in the LIBS emission and its effect decreases with the delay of analysis after the laser pulse. Therefore, the evaluation of the Stark broadening can be usually be performed by carefully selecting the right experimental conditions for minimizing the self-reversal of the line. Moreover, also in the presence of a moderate self-reversal, a meaningful estimation of the Stark broadening coefficient can be obtained, by only fitting the wings of the emission line, which are less affected by the self-absorption.

4. CONCLUSIONS

In this communication are summarized the results of a numerical experiment, aimed to the evaluation of the effect of plasma non-ideality on the experimental determination of the Stark broadening coefficient, one of the spectroscopic fundamental parameters of interest in plasma physics and chemistry.

We have demonstrated that a careful planning and optimization of the experimental conditions allows to obtain almost homogeneous plasmas and that, again under suitable hypotheses, the effect of the inhomogeneity does not affect critically the experimental evaluation of the Stark broadening coefficients.

These results are particularly important, because they allow the researchers to plan a LIBS experiment for the determination of the Stark broadening coefficients of plasma lines of different elements without the need of demonstrating again and again, through complex acquisition and manipulations of the LIBS spectra [Cirisan 2014], that the hypothesis of homogeneous plasma in LTE condition is fulfilled, in the proper time interval, in almost all the conventional LIBS experiments. Most of all, the reliability of the LIBS predictions can be easily checked through a careful analysis of the plasma emission lines, to determine the degree of self-absorption and minimizing its effect on the final results.

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